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NOUVELLE SÉRIE

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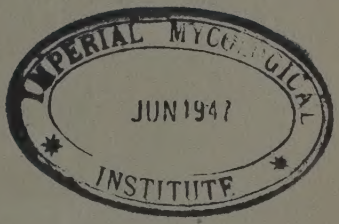

VOLUME XLV

№ 5

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THEORY OF ELASTICITY

SOME APPLICATIONS OF STATISTICS IN DESCRIBING DEFORMATION LAWS

By A. J. ISHLINSKY

(Communicated by N. E. Kochin, Member of the Academy, 15.III.1944)

The simplest laws describing the deformation of not altogether elastic and visco-plastic bodies involve linear relations between stress and strain and their derivatives with respect to time (1). Such are, for instance, the law of linear strengthening (2)

$$\sigma = E\varepsilon \quad \text{if} \quad \varepsilon < \alpha$$
$$\sigma = E\alpha + h(\varepsilon - \alpha) \quad \text{if} \quad \varepsilon > \alpha$$

and the law of after-effect and relaxation in the form (3)

$$\dot{\sigma} + r\sigma = b\dot{\varepsilon} + bn\varepsilon$$

Often, however, laws of this kind applied to some real bodies give no more than a merely qualitative description of their deformation.

But the deformation of real bodies can also be described quantitatively with sufficient accuracy if we conceive them as made up of a large number of elements obeying the simplest laws of deformation, with a given distribution of constants entering into the expression of these laws.

If a body supposed to be a fibrous structure is subjected to tension, the mean stress is described by the formula

$$\bar{\sigma} = \int_0^\infty \sigma p(\alpha)\, d\alpha$$

where α is a constant entering into the expression for deformation law of a single fibre, and $p(\alpha)$ is its distribution function. Thus, the product $Fp(\alpha)\,d\alpha$ represents that portion of the body's cross-section F which corresponds to the individual fibre whose constant ranges from α to $\alpha + d\alpha$.

If in the case of the first example the individual fibres obey the law of linear strengthening with different constants α, then the mean stress can be expressed as follows

$$\bar{\sigma} = \int_0^\varepsilon [E\alpha + h(\varepsilon - \alpha)]\, p(\alpha)\, d\alpha + \int_\varepsilon^\infty E\varepsilon p(\alpha)\, d\alpha$$

Hence

$$\frac{\partial^2 \bar{\sigma}}{\partial \varepsilon^2} = -(E - h)\, p(\varepsilon)$$

By means of the latter formula we can find the distribution function when the law of deformation of the body is known. Suppose that the hysteresis loop of an individual fibre has the shape shown in Fig. 1, and that the distribution function $p(\alpha)$ is constant if $0 < \alpha < \beta$, and is equal to zero if $\alpha > \beta$. Then the loop of hysteresis for the whole body is composed of portions of two parabolas (Fig. 2)

$$\bar{\sigma} = E\varepsilon \pm \frac{E}{4\beta}(a \mp \varepsilon)^2 \mp \frac{Ea^2}{2\beta}$$

where a is amplitude of strain variation ε. If a body of that kind is bearing an oscillating mass at one of its ends, while the other end is imbedded rigidly, then the decrease in amplitude by the end of a half-oscillation is

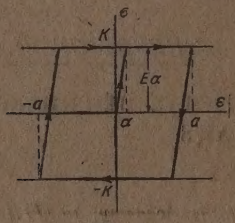

Fig. 1

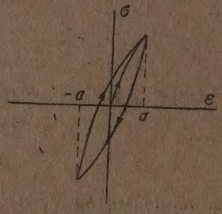

Fig. 2

approximately proportional to the squared amplitude at the beginning of a half-oscillation.

In another case, expressing the stress of individual fibres in the form

$$\sigma(t) = b\varepsilon(t) - \int_0^t b(r-n)\, e^{-r(t-\tau)}\varepsilon(\tau)\, d\tau$$

and taking the constants b and $bn/r = c$ to be equal in all fibres, while r and n, which are proportional to each other, are supposed to be different, we can arrive at the Boltzman-Wolterra inheritance law [4]

$$\bar{\sigma}(t) = b\varepsilon(t) - \int_0^t K(t-\tau)\varepsilon(\tau)\, d\tau$$

The relaxation core $K(t-\tau)$ is defined by the formula

$$K(x) = (b-c)\int_0^\infty re^{-rx}p(r)\, dr$$

where $p(r)$ is the distribution function of the constant r.

If

$$p(r) = 0 \quad \text{for} \quad 0 < r < a$$
$$p(r) = M/r^{2-\alpha} \quad \text{for} \quad a < r < \infty \qquad (0 < \alpha < 1),$$

then we have for small $t-\tau$ the approximate equation

$$K(t-\tau) = \frac{(b-c)\Gamma(\alpha)}{(t-\tau)^\alpha}$$

When the function $K(x)$ is given, the distribution function is found by means of Mellin's formula.

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15. III. 1944.

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PHYSICS

PIEZOELECTRIC TEXTURES

By A. V. SCHUBNIKOV, Corresponding Member of the Academy

The theory of piezoelectric crystals, as evolved by Voigt(1); is based on the assumption that there are linear relations between the components of the polarization vector I and those of the stress tensor t

$$I_1 = d_{11}t_{11} + d_{12}t_{22} + d_{13}t_{33} + d_{14}t_{23} + d_{15}t_{31} + d_{16}t_{12}$$
$$I_2 = d_{21}t_{11} + d_{22}t_{22} + d_{23}t_{33} + d_{24}t_{23} + d_{25}t_{31} + d_{26}t_{12}$$
$$I_3 = d_{31}t_{11} + d_{32}t_{22} + d_{33}t_{33} + d_{34}t_{23} + d_{35}t_{31} + d_{36}t_{12}$$

The totality of 18 constants, called piezoelectric moduli; forms a tensor of order three. In the general case of triclinic crystals without a centre of symmetry none of these constants is equal to zero. The conditions of symmetry in a suitable chosen system of coordinates will make some of the moduli vanish. And in the case of crystals having a centre of symmetry; all moduli are zeros; and in such crystals no piezoelectric effect can possibly take place.

In April 1940; while applying Voigt's theory to anisotropic not-single-crystal media; the author showed that piezoelectric phenomena could exist nowhere but in media of the following three types. The first type is characterized by the symmetry ∞ (one axis of infinite order); the second, by the symmetry $\infty \cdot m$ (one infinite axis with longitudinal planes of symmetry); and the third; by the symmetry $\infty : 2$ (one infinite axis and a set of transverse double axes).

The respective tensors of the piezoelectric moduli; referred to a rectangular system of coordinates so chosen that its third axis coincides with the infinite axis of the medium, have the following forms:

Type ∞						Type $\infty \cdot m$						Type $\infty : 2$					
0	0	0	d_{14}	d_{15}	0	0	0	0	0	d_{15}	0	0	0	0	d_{14}	0	0
0	0	0	d_{15}	$-d_{14}$	0	0	0	0	d_{15}	0	0	0	0	0	0	$-d_{14}$	0
d_{31}	d_{31}	d_{33}	0	0	0	d_{31}	d_{31}	d_{33}	0	0	0	0	0	0	0	0	0

The investigation of these groups of symmetry shows that in the media of types ∞ and $\infty \cdot m$ the infinite axes and all directions oblique to them are polar, which means that we can speak here of a forward and backward movement. Contrary to this, in the media of type $\infty : 2$ there are no polar directions at all.

The last conclusion on first consideration appears to be a double paradox. It implies, in the first place; that polar piezoelectric phenomena are possible in non-polar media. No such case is known in crystals. In crystals the absence of

polar directions involves the presence of a centre of symmetry; and the existence of a centre of symmetry is incompatible with the possibility of piezoelectric phenomena. In our case —and this is the second apparent paradox—we have no centre of symmetry, which does not mean in the least, however, that the medium must of necessity have polar directions. The identity between the absence of polar directions and the presence of a centre of symmetry; about which heretofore there was not a shadow of doubt; has now been found to be a wrong assumption. Whether piezoelectric phenomena may or may not take place in the media of type $\infty : 2$ is not decided by the presence or absence in them of polar directions; but rather depends upon the absence or presence of a centre of symmetry; or, in the end, upon all of their piezoelectric moduli being equal to zero or not.

This theoretical possibility of the occurrence of piezoelectric phenomena in non-polar anisotropic media called for a new approach to the problem of artificial production of piezoelectrics. Because before it had been tacitly assumed that piezoelectric phenomena could only take place in media of polar structure; *i. e.* in such that had all polar elements —whether dipole molecules or finished microscopic crystals —directed with like-charged ends toward one side; therefore the orientation of these elements could have only been attempted by polar means, for instance, by the application of an electric field. And this was the way taken by Eguchi [2], Meissner [3] and others who placed molten resin and other dielectrics solidifying on cooling in a strong electric field.

For obtaining non-polar piezoelectrics the application of an electric field was altogether unnecessary. Any mechanical way of orientating textural elements would do in principle equally well; provided they were needle-like or plate-like in form.

In my first attempts to obtain artificial non-polar dielectrics I used Rochelle salt, because the growing and practical use of Rochelle salt crystals was at the time experimented upon in our laboratory.

I expected to obtain good results with this substance because of its enjoying the following properties. The crystals of Rochelle salt are possessed of sharply expressed piezoelectric qualities. The salt melts readily (63° C). Under favourable conditions needle-like crystals form out of the melt.

On these considerations I suggested the use of an ordinary brush in preparing a piezoelectric. By means of the brush the melt was to be applied to some surface in parallel lines by leading the brush in one direction or in two opposite directions —forwards and backwards.

The first experiments with the brush were kindly taken upon by A. S. Shejin to whom I here wish to express my heartiest thanks. They were started in February, 1941; and proved to be a success. It was found that Rochelle salt plates of arbitrary area and thickness; possessing texture; can be prepared in this way. The material thus obtained looks like faience or porcelain and is easily worked with locksmith's or carpenter's tools. In response to mechanical stresses applied according to theory it displays a direct piezoelectric effect of considerable strength; and shows an inverse piezoelectric effect when electric field is applied in the direction determined by the theory.

In collaboration with A. S. Shejin the author has prepared piezoelements of varied form and size intended to work under different kind of stress —tension, bending, torsion, *etc.* It has been made clear by numerous tests that the new piezoelectric materials, to which they assigned the name of piezoelectric textures, are fitted in principle for practical use in manufacturing adapters; telephones; microphones, piezometers and other electric and acoustic equipment.

In July 1941 Shejin left me; but I went on experimenting until the middle of October with the assistance of F. A. Korolev. During this period we refined the conditions of manufacturing piezoelectric textures and established a phenomenon about the latter; which may be described as their ripening and which consists in a gradual increase of the piezoelectric modulus from zero (directly after the preparation of the piezoelement) up to a certain limit value and also in a gradual rise of ohmic resistance. Moreover; the voltaic sensitivity of the textures and of quartz was compared quantitatively in some tests of preliminary nature.

In the period between November 1941 and March 1943 I had limited possibilities for pursuing the experiments with piezoelectric textures and worked mainly at the theory of this problem. It is during this time that I wrote a monograph entitled «Piezoelectric Textures», which is now in press. In this monograph various possible types of texture—piezoelectric and otherwise—are discussed in detail; and the notion of second kind piezoelectric texture is established for textures with needles arranged parallel to one plane. Later such textures were materialized in practice. The book also deals with the geometric conditions for the formation of different kinds of texture, investigates the characteristic features of piezoelectric tensors; derives the properties of the textures from the properties of the crystals composing them, and considers many other theoretical problems bearing on textures.

Lately I was able to show that plywood has the properties of a piezoelectric texture of the first kind.

After the experimental work on piezoelectrics was resumed, F. A. Korolev under the participation of B. A. Fersman mounted an apparatus for measuring piezoelectric moduli quantitatively, and by means of it showed that for some textures their modulus d_{14} is fifteen times as great as the modulus d_{11} of quartz.

Further work—it may be expected—will lead to the use of piezoelectric textures for various practical purposes.

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6.IV.1944.

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GEOPHYSICS

ON SEISMIC LOGGING

By A. E. OSTROVSKY

(Communicated by S. L. Soboleff, Member of the Academy, 5. IV. 1944)

Among the geophysic methods of prospecting for oil, the electric logging of bore-wells holds the most firmly established place. The logging diagrams give a characteristic of the lithological profile and furnish some evidence as to the oil-storing properties of the drilled rocks. They make it possible therefore to conduct drilling without taking core samples and thus save time. By now this method is generally adopted in the oil districts of this country.

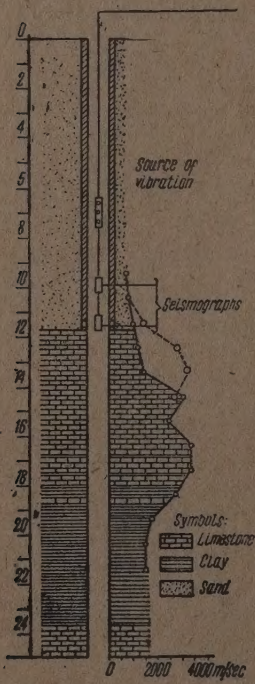

Fig. 1

But in the case of oil fields of carbonate type such as those of the Second Baku, the differentiation of oil-bearing rocks by means of electric logging is a matter of considerable difficulty. Here the electric resistance of dense limestones differs little from that of their porous facies which are the oil-stored rocks of the productive layer.

On the other hand, oil and limestone differ greatly in elastic properties. This circumstance suggests the use of seismic logging for the differentiation of oil saturated horizons.

Yet, the practical application of this method presents various difficulties. In the first place, there is the necessity of measuring the time difference of the travel of seismic waves with an accuracy up to 10^{-3} sec., and then the propagation of these waves when there is a bore-well presents a rather complicated picture. In fact, their way in this case runs through the drilling mud, the casing, the ground and so on. And on certain ways both longitudinal and transverse waves travel along.

These problems engaged the attention of the present author in the period from 1938 to 1942. I began experimenting with a test-well drilled 25 m deep on the territory of the Seismological Institute, Moscow, and afterwards continued the experiments on one of this country's oil-fields. The geological section of the test-well is shown in Fig. 1.

The essential difference of the method adopted in these experiments from the usual procedure of seismic logging is that: 1) the source of oscillations is placed directly into the well, and owing to this by far more clear-cut arrival times are

obtained; 2) two closely located seismographs are used for recording, and the velocity diagram of the wells is built up from the difference between the time of the waves' travel to these seismographs.

It may also be remarked that the existence of a large number of different waves moving in the well simultaneously precludes the measuring of small time differences according to the impulse method.

Instruments. In carrying out the experiments vertical well-seismographs were used. They are smaller in size compared to the ordinary well-apparatus, and provided with a special suspender of the pendulum by means of which the period of the seismograph can be regulated. As a source for the excitation of oscillations an ordinary electric blasting cap was employed, because work with shooting perforators suggested the use of this method for exciting elastic oscillations also at great depths.

For blasting several electric blasting cap a special capsule with cavities was used. The operation scheme of this device was calculated to permit 10 detonators be exploded in succession without once taking out the capsule from the well.

It should be noted that, owing to the strong destructive effect of electrodetonators, the cavities of the capsule are demolished, and it is only by a suitable choice of steel and a thermal treatment that I was able to obtain a capsule that withstood a large number of explosions in one cavity without being seriously damaged.

Before starting the observations the devices involved were arranged in the following order. Two seismographs were lowered into the well, one located 1 to 5 m higher than the other. Two or three metres above them a cartridge for exploding the electric blasting cap was placed. The records were taken by Siemens oscillograph provided with an automatic contrivance for switching-in the explosion circuit synchronously at the instant the shutter of the place-holder with revolving cylinder is closed. The travel time of the wave was counted by means of a comparator with optical magnification.

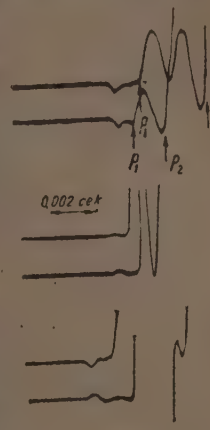

Fig. 2

By this method of recording and treatment it is possible to measure the velocity on a basis of 1 m as accurately as up to 3—5 per cent.

Results of Experiments with Test-Well. Fig. 2 presents seismograms obtained by blasting the electric blasting cap at different depths in the well. The first (bottom) seismogram corresponds to a depth of 21 m—a layer of clay. The second refers to a limestone layer and the third (top), to coarse-grained sand with pebbles. The propagation velocity of elastic waves is 1350 m per second on the first seismogram, and 2420 m per second, on the second seismogram. The third seismogram has two distinct phases: p_1 and p_2. The first seismogram gives a wave travelling with a velocity of 3500 m per second; and the second, a wave that arrived with a velocity of 900 m per second. The first phase was observed only in the upper (provided with a casing) part of the well. Apparently, this arrival time is due to the wave moving along the casing. Its velocity approaches very closely to that of transverse oscillations in steel. The second phase is the arrival time of the elastic waves (probably, the transverse waves) moving across the ground—sand with pebbles.

Upon careful examination it may be seen that before the arrival p_1 there are oscillations that arrived with a velocity higher than 3500 m per second. The first arrival time of these waves cannot be counted off on the seismogram on account of the insignificant energy; yet, the fact that they were first to arrive seems to mean that they are longitudinal waves that propagated along the wall of the casing. Their velocity should not be lower than 5000 m per second. The frequency of these oscillations is very high, about 5000 to 10 000 periods per second, and their amplitude is tens of times as low as the amplitude of transverse waves—the radial vibrations of the casing. The transverse waves moving along the casing with a velocity of

3500 m per second have a frequency and an amplitude tens of times as small as the waves travelling across the ground. The amplitude of the latter reaches far beyond the paper-area of the seismogram.

A decrease in the sensitivity of the galvanometer causes the phase p_1 to disappear altogether.

Before the arrival time of the elastic waves a small impulse is observed on the seismogram, which is due to the influence of the switching-in of the current that calls forth the blasting of the electric blasting cap.

A conclusion very important from the practical point of view can be drawn from these observations: the thickness of the casing being small in comparison with the length of the elastic waves, the seismic energy transmitted by the casing is by far smaller than that of the waves travelling across the ground. It will be obvious that the presence of a casing does not present any difficulties in measuring the velocity in the rocks across which the well has been sunk.

By decreasing the sensitivity of the apparatus 10—20 times and using a galvanometer with a lower period of proper oscillations it was found possible to remove from the seismogram the waves passing across the casing, and thus to obtain clear-cut arrival times for the waves propagating across the ground.

By means of the method described the author constructed the velocity diagram for the profile of the well in a way in which the electric resistance diagram is usually constructed (Fig. 1).

It may be seen by comparing this diagram with the geological section that the velocity shows a strong increase within the limestone layer; reaching here 3200 m per second. If we were to mark out the upper and the lower boundary of the limestones from the data of the diagram, we would have found the limestone layer to be displaced 2 m downwards against its actual depth. This divergence may not be explained away by supposing that the limestones are weak where they border upon the sand and are therefore characterized by lower velocity of the waves. On the contrary; the upper boundary of the limestone is remarkably «hard».

Moreover; the velocity diagram obtained for the same values with the same arrangement of the instruments but with a source placed below them (dotted line in Fig. 1) turned out to be displaced upwards, with respect to the division lines of the layers; by the same value.

Therefore for observations conducted in wells the measured velocity must be referred to the middle point of the distance between the shot-point and the more remote instrument. To explain this circumstance a series of additional investigations have to be carried out. Measurements in the same well; when the distance between the seismographs had increased up to 3—5 m, showed that the longer this distance, the less distinct on the diagram are the velocities corresponding to small layers.

In order to record a limestone layer 5 m thick, the instruments must be placed one to two metres apart from each other. Hence the distance between the instruments should be two-three times less than the thickness of the layer in which the velocity is measured.

About the middle of the layer of limestone the velocity shows a decrease. Repeated measurements at this place went only to confirm this phenomenon; and comparisons with the data of the drilling-records showed that the limestone layer was not homogeneous and was less strong in this part.

As is seen from the diagram, the velocity values are lower than in the case of longitudinal waves that were observed upon seismic prospecting, while determining the mean velocity with the well-seismograph in the usual way. This may hardly be accounted for by the peculiarities of the rocks in that region. Comparing the obtained velocity with those observed in the same rock upon seismic prospecting we see a decrease by as much as 1.5—2 times. This leads us to suppose that the arrival times marked out upon the seismograms correspond to a transverse wave moving along the stem of the well in the form of radial oscillations. The energy of these oscillations like the energy of transverse oscillations in a casing seems to be incomparably greater than the energy of the longitudinal waves.

Conclusions

1. The method described here makes it possible to measure the velocity of transverse waves with an accuracy sufficient for the practice.

2. Seismic logging is possible in wells provided with casing.

3. By means of the velocity diagram the rocks not only can be differentiated according to their lithological composition, but in some rocks portions differing in physical-mechanical properties can also be distinguished.

4. The measurements of the velocity are to be referred to the middle of the distance between the shot-point and the more remote seismograph.

The method was also tried in deep wells of an oil field. In these tests seismographs of a special design have been used fitted for work at a high hydrostatic pressure. There was also made an analysis of electric influences arising from the use of a probe with two instruments fastened to a single cable (about 1 km long); a scheme was calculated with the object to get rid of these influences.

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CHEMISTRY

SOLUTION HEAT POLYTHERMS FOR SALTS OF LOW CONCENTRATIONS

By N. K. VOSKRESENSKAYA and K. S. PONOMAREVA

(Communicated by I. I. Černjaev, Member of the Academy, 16. III. 1944)

The question of the influence of temperature on the heat of solution of salts was raised by the first investigators of this property, but little progress has been made since their times.

Graham (1) found in the year 1844 that the amount of heat absorbed in solution decreased with increasing temperature. Person (2) studied the influence of temperature on the solution heat in more detail and connected it with the specific heat of the solution; of water and of the solid salt.

In the literature of last decades no data on the direct measurements of the heat of solution with reference to temperature appear to have been reported; except for a narrow interval of temperatures (12 to 25° C) (3).

That the process of solution becomes more exothermal * as the temperature grows; follows from Kirchhoff's equation, which in the case of solutions takes the form(4):

$$dL_c/dT = c_{\text{solid}} - \Phi \qquad (\Phi < c_{\text{solid}})$$

where Φ is the apparent molar specific heat of the salt; and c_{solid} is the molar specific heat of the solid salt.

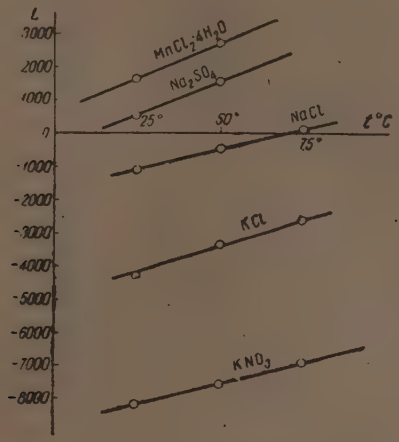
One cannot decide owing to the lack of data whether the negative heat of solution becomes positive when the temperature is raised high enough.

The authors have measured the heat of solution of KCl; NaCl and KNO_3 for 25; 50 and 75° C, and of $MnCl_2 \cdot 4H_2O$ and Na_2SO_4 for 25 and 50° C. The concentration of the dissolved salt in all cases save that of NaCl corresponded to a ratio of 3.33 moles of salt to 1000 moles of water. In the case of NaCl the concentration was two times at high because of the smaller heat of solution of this salt.

The measurements were carried out in a calorimeter provided with a isothermal shell which has been described earlier by the authors (5). The salt sample was placed in a glass flask fastened inside the calorimetric beaker. The flask contained a rod with a mercury seal. At the required instant the bottom of the flask was broken by means of this rod and the salt dissolved. No less than two determinations were made in each case. After the solution test; the water value of the calorimetric system was determined by the method of electric heating (5). The accuracy of the solution heat determinations ranged within about 0.5 per cent in general; but not in the case of NaCl where the error was somewhat higher; owing to the smallness of the measured quantities.

* «More exothermal» means that the exothermal effects increase at the expense of the endothermal.

All salts were recrystallized: $MnCl_2 \cdot 4H_2O$ was kept in a exsiccator over 50 per cent H_2SO_4. Analysis for water gave 36.50 per cent instead of the 36.41 per cent computed theoretically. Na_2SO_4 was obtained by dehydration of $Na_2SO_4 \cdot 10\,H_2O$ at 140° C.



The data obtained are given in the adjoined table and represented graphically in the figure.

Solution Heats at Different Temperatures

Salt	Temperature		
	25°	50°	75°
NaCl	—1044	— 444	+ 117
KCl	—4209	—3324	—2609
KNO_3	—8185	—7590	—6928
$MnCl_2 \cdot 4H_2O$	+1730	+2768	
Na_2SO_4	+ 580	+1596	

As the temperature goes up, the solution process in the case of all tested salts becomes more exothermal. The polytherms are straight lines.

The solution heat of NaCl changes sign in the vicinity of 70° C, and dissolves with evolution of heat when a temperature of 75° C is reached.

The fact that the process becomes more exothermal with increasing temperature is connected with the growing share of the hydration effect in the heat of solution. This effect, like all other possible positive summands of the heat of solution (such as the heat of formation of ionic pairs and the heat of formation of a complex), is bound to decrease in absolute value with increasing temperature. Therefore its increase in our case is merely a relative one and a consequence of a decrease of the negative summands entering into the heat of solution. The main negative summand (the energy of the lattice) varies but slightly with temperature. Its decrease (which can roughly be estimated by means of Born's equation through the substitution of values of r corresponding to different temperatures (⁶)) is too small to account for the observed increase in the exothermicity of the solution process.

In our opinion the observed changes in the heat of solution can be explained

in terms of the quasi-crystalline structure of water ([7]). We have once used this conception in studying the specific heat of solutions ([8]).

There can be no doubt but that an increase of temperature is apt to shift the equilibrium

$$\text{water I} \rightleftarrows \text{water II} \rightleftarrows \text{water III} \qquad (1)$$

toward the right; which fact is reflected in various properties of water ([9–14]).

In dissolving electrolytes which act on the structure of water like the increase in temperature; heat is expended upon shifting the equilibrium (1) toward the right.

Bernal and Fowler ([7]); followed by Eley and Evans ([13]), in computing the first heat of solution, took account of the energy absorbed in the breaking of bonds involved in the tetrahedral structure of water.

The negative summand of the heat of solution; connected with the shifting of equilibrium (1) to the right; should diminish with increasing temperature, because equilibrium (1) is already shifted to the right even in pure water. This summand increases more rapidly compared to the effect of hydration, and the latter therefore gains in weight as the temperature goes up.

The largest angle with the abscissa is formed by the polytherms of $MnCl_2 \cdot 4H_2O$ and Na_2SO_4, which salts have also the highest ionic power. The rest form the following decreasing sequence if arranged with reference to the angle of slope of their polytherms to the axis of abscissae;

$$KCl > NaCl > KNO_3$$

These three salts have been found to follow in the same succession when compared with reference to other properties — entropy ([13]), temperature of maximum density ([14]), specific heat of solutions' water ([8]). This succession was looked upon by us as an anomaly, not fitting within the frame of general regularities. It points to the existence of subtle differences between the behaviour of Na^+ and K^+ ions in water; which are difficult to explain at this juncture.

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CHEMISTRY

ON TWO NEW COMPOUNDS OF CYTISINE

By M. V. TSAREV

(Communicated by N. D. Zelinsky, Member of the Academy, 10. IV. 1944)

Cytisine, $C_{11}H_{14}ON_2$, is a crystalline alkaloid; discovered in 1862 by Scott-Grey. Its structure was established by Späth and Ing in 1932. As a medicine it was first applied by Mashkowsky (1) in 1940.

Cytisine gives well crystallizing salts, such as the hydrochloride, hydrobromide, hydroiodide, sulphate, nitrate and a series of compounds in the form of double salts of the hydrochlorides with chlorides of heavy metals. A series of derivatives has been described in which participates the secondary amino-group; such as methyl-, ethyl- and isobutyl-cytisine, as well as benzoyl-cytisine. The latter is easily soluble in water, alcohol and chloroform and insoluble in diethyl ether (2).

As there exists no method for the quantitative determination of cytisine, the author undertook a search for its derivatives with the participation of the secondary nitrogen atom that would be insoluble in water; and that could be used for the determination of cytisine. Such a direction in research was due to the fact that plants in which cytisine is found, *Thermopsis lanceolata* (3, 4) and *Genista tinctoria* (5); contain alkaloids having a nitrogen belonging to a tertiary amine.

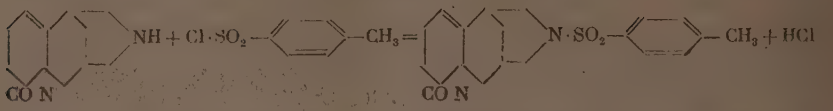
As a result of the reaction of cytisine with *p*- toluene-sulphonyl - chloride and with α-naphthalene-sulphonyl-chloride two new crystalline compounds have been prepared—*p*-toluene-sulphonyl-cytisine $NC_{11}H_{13}ON.SO_2C_7H_7$ and α-naphthalene-sulphonyl-cytisine $NC_{11}H_{13}ON.SO_2.C_{10}H_7$. Owing to their poor solubility in water; it was possible to develop a method of quantitative analysis of cytisine.

Preparation of *p*-toluene-sulphonyl-cytisine

A weighed sample of cytisine, about 0.1 g (1 mol) is dissolved in 2.5 cm³ of an aqueous solution of 1 *N* KOH (4 mol). To the alkaline solution of cytisine 5 cm³ of an ether solution of *p*-toluene-sulphonyl-chloride containing 0.3 g of the substance (3 mol) are added. The water-ether mixture is shaken for 10 min. The flask is placed on a warm water bath, air is bubbled through in order to eliminate the ether and the flask is rotated so that crystals that separate as the ether evaporates remain in the liquid. The flask is fitted with a reflux condenser, and then placed for one hour on a boiling water bath in order to decompose the excess of the reagent. The medium should be feebly alkaline.

After heating the flask is left at room temperature until the next day. The poorly soluble precipitate of *p*-toluene-sulphonyl-cytisine is transferred quantitatively into a weighed glass-filter where it is washed free of the reaction products $C_7H_7SO_3K$, KCl and KOH with distilled water. The crystals are dried together with the filter at 95—100° to constant weight.

The reaction of *p*-toluene-sulphonyl-chloride with cytisine can be expressed as follows:



The crystalline compound *p*-toluene-sulphonyl-cytisine has been characterized.

Analysis

6.400 mg subst.	0.461 cm³ N_2	(731 mm, 13°)
4.875 » »	0.343 » N_2	(740 » 13°)
3.789 » »	2.573 mg $BaSO_4$	
7.546 » »	5.016 » $BaSO_4$	

Found %: N 8.28; 8.18; S. 9.32; 9.13;

$C_{18}H_{20}O_3N_2S$. Calculated %: N 8.14 S 9.31

The melting point of *p*-toluene-sulphonyl-cytisine is 204—205°. It crystallizes perfectly from a mixture of acetone and ether; as well as from a large volume of water; is very well soluble in 25 per cent HCl; well soluble in chloroform and acetone and badly soluble in water. One part of *p*-toluene-sulphonyl-cytisine is soluble in 1625 parts of water at 15° C, in 1507 parts at 25° C and in 205 parts of boiling water.

If one observes the conditions described above for the preparation of *p*-toluene-sulphonyl-cytisine as a method for the quantitave determination of cytisine, it is absolutely necessary to take into consideration the amount of the filtrate obtained from washing the crystals with water on the filter and to introduce a correction into the weight of the precipitate on the solubility of *p*-toluene-sulphonyl-cytisine. This correction is obtained by multiplying the amount of the filtrate in cm³ by 0.0025.

According to this method, a series of quantitative determinations of cytisine in a pure preparation has been carried out.

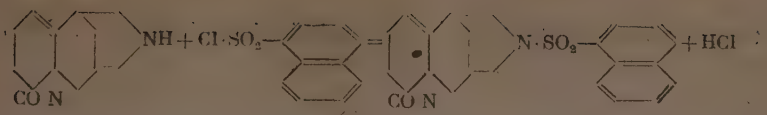
Weighed portion of $C_{11}H_{14}ON_2$	in gs:	0.1137; 0.1147; 0.0941; 0.0892
Obtained $C_{18}H_{20}O_3N_2S$	in gs:	0.2025; 0.2015; 0.1656; 0.1580
Found cytisine	in %:	98.33; 96.08; 97.12; 97.75

Preparation of α-naphthalene-sulphonyl-cytisine

To a weighed sample of about 0.1 g of cytisine are added 3 cm³ of 1 *N* KOH; 0.3 g of α-naphthalene-sulphonyl-chloride dissolved in 5 cm³ of diethyl ether and 1—2 drops of methyl-red. The flask is stoppered with a cork and an air reflux condenser and placed on a hot water bath.

As the ether evaporates an amorphous resin-like precipitate is formed which solidifies in 5—10 minutes. After the elimination of the ether the flask is maintained for 1 hour at 90—95° watching all the time so as to have in the flask about 5—7 cm³ of the liquid, therefore adding water into the flask. The content of the flask is left standing until next day, α-naphthalene-sulphonyl-cytisine is quantitatively transferred into a weighed glass-filter, washed with 20—30 cm³ of water and dried at 95—100° C to constant weight.

The reaction of α-naphthalene-sulphonyl-chloride with cytisine can be expressed by the following equation:



A crystalline compound α-naphthalene-sulphonyl-cytisine has been obtained.

Analysis

6.690 mg subst.	0.433 cm³ N_2	(725 mm, 14°)
6.840 » »	0.451 » N_2	(725 » 14°)
5.142 » »	3.210 mg $BaSO_4$	
7.482 » »	4.610 » $BaSO_4$	

Found %: N 7.36; 7.50; S 8.57; 8.46

$C_{21}H_{20}O_3N_2S$. Calculated %: N 7.37; S 8.43

α-naphthalene-sulphonyl-cytisine is a crystalline substance having a m. p. 229—230°. It crystallizes perfectly from ethyl acetate and well from benzene; dichloroethane and petroleum ether. From acetone it crystallizes only after the addition of water. It is poorly soluble in water: one part of α-naphthalene-sulphonyl-cytisine dissolves in 6620 parts of water at 15° and in 1100 parts at 100° C.

Owing to the extremely poor solubility of α-naphthalene-sulphonyl-cytisine in water, it is the intention of the author to determine cytisine quantitatively in the form of this compound.

From the amount of α-naphthalene-sulphonyl-cytisine obtained the amount of cytisine is calculated by means of the formula:

$$X = \frac{A \cdot 0.5 \cdot 100}{B}$$

where X is cytisine per cent; A; weight of naphthalene-sulphonyl-cytisine; B, weight of the sample used.

Results of the gravitational analysis of cytisine using α-naphthalene-sulphonyl-cytisine, according to the method described, are given below.

Weighed portion $C_{11}H_{14}ON_2$ in gs:	0.1325;	0.1167;	0.1041;	0.1062;	0.0918
Obtained $C_{21}H_{20}O_3N_2S$ in gs:	0.2588;	0.2282;	0.2014;	0.2070;	0.1834
Found cytisine in %:	97.00;	97.76;	96.73;	97.40;	99.80

The author wishes to acknowledge his appreciation to Prof. V. V. Feofilaktov for direct help in the work.

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PHYSICAL CHEMISTRY

A STATISTICAL THEORY OF ADSORPTION ISOBARS AND ISOSTERES FOR NON-UNIFORM SURFACES AND A GRAPHICAL METHOD OF FINDING THE DISTRIBUTION FROM THE ISOTHERMS AND ISOBARS

By S. Z. ROGINSKY, Corresponding Member of the Academy

In a previous communication (1) we developed a simplified method based on the fact that the surface covering rapidly diminishes with a decrease in the heat of adsorption, which is equally effective for deriving the adsorption isotherms from the distribution of the surface areas with respect to heats of adsorption and *vice versa*. The fundamental result of that was two general formulae: (4a) (1) for isotherms and (10) (10a) (1) for distribution.

The relation between Q and p is given by the equation:

$$Q = -RT \ln (p/b_0) \qquad (1)$$

where Q is the heat corresponding to the point of inflexion of the boundary line between the free and occupied areas of the surface on the distribution graph $\rho_Q = \rho(Q)$, and b_0 is a constant of the formula connecting the sorption coefficient b in the Langmuir equation with the heat of adsorption

$$\theta = \frac{p}{p+b}; \qquad b = b_0 \exp(-Q/RT)$$

θ is the specific covering. An analysis of the accuracy of our approximate method reveals that for $q = q(p)$ the following approximation is equal:

$$q = q(p) = \gamma \int_{Q}^{Q_{max}} \rho_Q \, dQ - {}^2/_3 \gamma RT^2 \frac{d\rho}{dQ}. \qquad (2)$$

For the distribution a more exact solution leads to

$$\rho_Q = \frac{dq}{\gamma RT d \ln p} - \frac{2}{3} \frac{d^2q}{\gamma RT (d \ln p)^2} \qquad (3)$$

and hence, thanks to the internal compensation of the corrections, our first approximation coincides with the second, and therefore it should be a good approximation in those cases, where the deviations from the laws of adsorption that held for simple surfaces are due to the presence of extensive distribution with respect to heats of sorption.

Such an accuracy of result lends interest to the application of the method to the isobars $q = q(T)$ at $p = \text{const}$, and the isosteres $p = p(T)$ at $q = \text{const}$.

Our method of solving the problem is based on an analysis of the influence of the corresponding parameters on the boundary line.

In Fig. 1 there is shown in the coordinates θ and Q and, correspondingly, ρ and Q the change in the boundary with an increase in T. The condition as we interpret it, means keeping constant the position of the point of inflexion

in which $\theta = 0.5$; *i. e.* the boundary heat of sorption remains constant. With a change in T; the boundary curve appears to turn around this point, stretching out somewhat along the axis of abscissae. In the case of our approximation equation (4) with $Q = \text{const}$ holds for all isotherms:

$$p = b_0 e^{-Q/RT} = b_0 e^{-\text{const}/RT} \qquad (4)$$

Upon passing to new temperatures the only thing that changes in this equation is the denominator of the fraction forming the exponent of the expression. This equation is actually the equation of the isostere with Q corresponding to $\theta = 0.5$. Comparison of Q at different q gives, consequently,

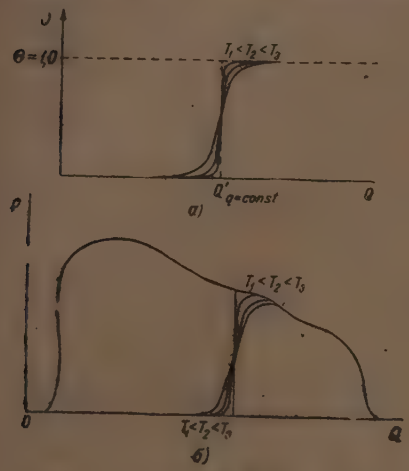

Fig. 1. Isosteres $\dfrac{\partial \ln p_T}{\partial T} = \dfrac{Q_{\theta=0.5}}{RT^2}$

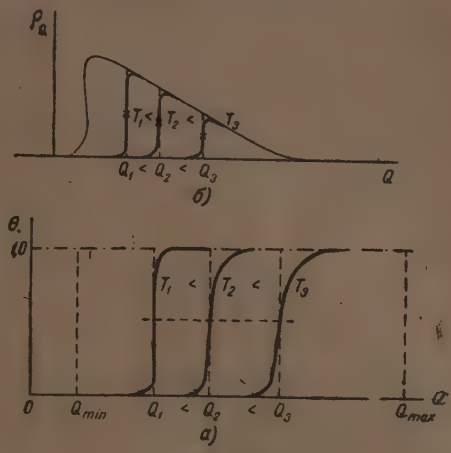

Fig. 2. Isobars $\dfrac{Q_1}{T_1} = \dfrac{Q_2}{T_2} = \dfrac{Q_3}{T_3} = \text{const}$

a curve of the differential heats. The graphs of $\theta = \theta(Q)$ and $\rho = \rho(Q)$ at constant p are given in Fig. 2, *a* and *б*, respectively. From the condition

$$p = b_0 e^{-Q/RT} = \text{const} \qquad (4a)$$

it is clear that characteristic for the isobar is the equality

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \ldots = \frac{Q}{T} = \text{const} = C \qquad (5)$$

In the isobar the boundary heat of sorption increases with a rise in temperature. The entire boundary curve is shifted in the direction of higher heat values, stretching symmetrically along the axis of abscissae.

The dependence of q upon $\rho(Q)$ is given by an equation that is a complete analogue of equation (4a) [1]

$$q_{p=\text{const}} = \gamma \int_{Q}^{Q_{max}} \rho_Q \, dQ \qquad (6)$$

with the normalization $Q/T = C$. The converse problem of finding ρ_Q from q again reduces to differentiation with respect to Q. Put $\gamma = 1$, then

$$\rho_Q = -\frac{dq}{dQ} = -\frac{dq}{dT}\frac{dT}{dQ} \qquad (7)$$

or, employing the obvious equalities

$$\frac{dT}{dQ} = \frac{d}{dQ}\left(\frac{Q}{C}\right) = \frac{1}{C} = \frac{T}{Q} = -\left[R \ln \frac{p}{b_0}\right]^{-1} \qquad (7a)$$

we get:

$$\rho_Q = -\frac{1}{C}\frac{dq}{dT} = \frac{1}{R \ln (p/b_0)}\frac{dq}{dT} = -\frac{dq}{Qd \ln T} \qquad (8)$$

Substituting into equation (6) different values of ρ_Q, we get:

α. At $\rho_Q = H(Q_{max} - Q)^n$.

$$q = H\int_{Q}^{Q_{max}} (Q_{max} - Q)^n = \frac{H}{n+1}(Q_{max} - Q)^{n+1} = \frac{H}{n+1}(Q_{max} - CT)^{n+1}$$

or

$$q = [q_0 - \beta T]^{n+1} \tag{9}$$

with the particular solution for $n=0$, *i. e.* for $\rho_Q = H$.

$$q = q_0 - \beta T \tag{9a}$$

β. At $\rho_Q = H\exp(-\alpha Q)$. Substitution of this ρ_Q into (6) with subsequent integration with the replacement of Q by CT from (5) leads to the equation

$$q \cong ae^{-\beta T} \tag{10}$$

As an example of the converse problem, let us find the distribution for the logarithmic isobar

$$q = q_0 + a \ln T \tag{11}$$

Making use of (8), let us differentiate it with respect to $\ln T$. This gives:

$$\rho_Q = H/Q, \text{ where } H = a. \tag{12}$$

Equations (10), (10a) [1] and (8) are remarkable in that they may be directly utilized in an analysis of experimental data without preliminary fitting of an equation for the isotherm or the isobar. As a matter of fact, according to the generally known property of derivatives, ρ_Q for isotherms with an accuracy to a constant is equal to the slope of the curve $q = q(\ln p)$ at a given point. For an isobar the same holds for the derivative of q with respect to the temperature. Therefore having plotted the graph $q = q(T)$ from experimental data or, correspondingly, $q = q(\ln p)$, we by graphical differentiation immediately find in a certain arbitrary scale the shape of the distribution function. If the distribution, regardless of the geometric form, is broad, the result is reliable; if it corresponds to a narrow band, the result has only a qualitative meaning, since the narrower the distribution; the more marked is the diffusion of the order $2RT$, connected with the nature of the approximation made. For the same reason the close-lying maximums of the function on ρ_Q should merge into one broader maximum.

Application of our method is restricted to convex isotherms and a sufficiently broad distribution. Thus; it is not expedient to consider distributions close to a uniform value or with a small absolute value of the fraction Q/RT. On the other hand, there is nothing to interfere with its application to the adsorption of mixtures on highly non-uniform complex surfaces. New here is only the possibility of the appearance of two separate steep boundary lines. The exponential relation between the velocity and the energy of activation makes possible an analogous interpretation of reaction activity on complex catalytic surfaces, their poisoning, *etc.* A complete theory of the rate of activated sorption is easily obtained. It becomes possible to obtain a number of interesting results, including a precise classification of kinetic types; for the kinetics of catalytic reactions. In all these complex cases scientific analysis reduces to a comparison of the energy characteristics of sorption Q_1, Q_2 *etc.* and the energy of activation E_1, E_2, *etc.* and their functional connexion, reducing to an analysis of the relation of the types of statistical distribution with respect to these quantities. This part of our work will be dealt with in greater detail in separate communications.

In conclusion I note the fruitful influence on the development of these investigations of the discussion of relevent statistical problems with O. M. Todes, Docton of Chemical Sciences.

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BIOCHEMISTRY

ENZYMATIC ACTIVITY OF CARBONIC ANHYDRASE

By E. M. KREPS

(Communicated by L. A. Orbeli, Member of the Academy, 20. IV. 1944)

The conception of the turn-over number has proved useful for the quantitative evaluation of the catalytic efficiency of enzymes. For each molecule of substrate transformed the enzyme undergoes one complete cycle.

The turn-over number is defined as the number of cycles per minute which the enzyme undergoes.

The vital importance of the chemical reactions catalyzed by carbonic anhydrase and its rather high concentration in blood (1 gram per liter of blood) suggest to make a quantitative evaluation of the enzymatic activity of carbonic anhydrase and to compare it with other enzymes.

For a quantitative estimation of the turn-over number of carbonic anhydrase the hydration reaction was used. Several assumptions were made in order to simplify the calculations. The results obtained may represent the lower limit of the activity value.

The velocity of the hydration reaction depends on temperature; CO_2 tension, pH of the milieu; and the presence of activators. The measurements were made by the Brinkmen method.

The initial CO_2 concentration was $m/400$, the temperature of the reaction 0°, pH ranged from 8.4 at the beginning to 7.0 when the end-point was reached. According to Kiese and Hastings (1), at such pH values the reaction velocity is at its maximum and nearly constant.

The enzyme concentration was much lower as compared with natural conditions. The blood had to be diluted 1 : 8000, in order to decrease the velocity of the reaction and to make it measurable by simple methods. The conditions within the intact red blood cell must, of course, be quite different from those in the highly diluted haemolyzed blood.

The calculation of the enzymatic activity was based on the following data.

Substrate: 1 ml of $m/200$ CO_2 solution containing $0.5 \cdot 10^{-5} = 5$ micromols CO_2.

Enzyme: 0.05 ml of human blood equivalent to $\frac{3.3 \cdot 5}{100 - 200} = 82.5 \cdot 10^{-5}$ micrograms Zn = $1.3 \cdot 10^{-5}$ microgram-atoms Zn = $1.3 \cdot 10^{-5}$ micromols of carbonic anhydrase.

The non-catalyzed reaction attains the end-point in 120 sec. The catalyzed reaction takes only 30 sec. The velocity of the reaction is at its maximum at the beginning and decreases rapidly as the reaction proceeds along a steep curve. Taking the whole reaction time, we get a value which is obviously lower than the true one.

This permits us to take no account of the insignificant part of the substrate which undergoes the non-catalyzed hydration.

Thus, one molecule of the enzyme corresponds to $\frac{3}{1.3 \cdot 10^{-5}} = \text{ca } 0.4 \cdot 10^5$ molecules of the substrate transformed in 30 sec. The turn-over number or the number of cycles per minute is thus equal to ca 10^6 at 0°.

Most of the enzymes studied have a much lower catalytic activity. Only the catalase possesses a turn-over number of the same order of magnitude; ca $2.4 \cdot 10^6$([5]). Both enzymes, catalase and carboanhydrase; have some features in common. Both are metal protein enzymes; both catalyze reactions in which only simple molecules as H_2O_2, H_2O; O_2 or CO_2 are involved. When ranged according to enzymatic activity; carbonic anhydrase takes its place among the most active of the enzymes.

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GEOLOGY

EVIDENCE ON THE STRATIGRAPHY OF THE TERTIARY DEPOSITS OF THE ALAI RANGE

By O. S. VIALOV

(Communicated by W. A. Obruchev, Member of the Academy, 27. III. 1944)

The Tertiary deposits of the eastern part of the Alai Range should be considered as utterly unexplored, although they have been dealt with by many investigators. Many papers described definite sections of the Palaeogene, but the descriptions are always too schematic and are lacking any stratigraphical subdivision. From these descriptions it is not possible to reduce them to the unique stratigraphical scheme which has been worked out for Central Asia (1).

In 1943 the writer had the opportunity on his way to the Pamir to examine several sections of the Palaeogene exposed at the Pamir route.

At the meridian of the town of Osh three main belts of development of Cretaceous and Tertiary deposits can be traced in the Alai Range. As it has been at present ascertained, the sections of these three belts are built up in a different manner. Each of them will therefore be described separately.

The author has examined the exposures near the Gulcha fortifications, at Kizyl-Kurgan and Kunek-Sogdy, south of Sufi-Kurgan.

The description of the first section has been more than once given in literature, many travellers having passed *via* Gulcha to the Pamir or to Kashgar. None of these descriptions can, however, give any idea as to the structure of the Tertiary section.

A cursory inspection of the rather poor exposures on the right bank of the Gulcha River revealed the following picture. Upon the thick Goznau gypsum series of the Danian (and Burkhara?) stage rest white, porous, frequently breccia-like limestones and farinaceous dolomites (~60 m). They undoubtedly refer to the Bukhara stage.

These are followed by deposits of the Suzak stage, in which no fauna has been discovered. Over the Bukhara limestones there is a covered slope, in which in the ground dug out of marmot holes green and red clays are visible (10—15 m). Higher up there is a cornice of sandstones; now white and yellow, and now red and pink; passing into gravel beds and containing ripples of gravel (8—10 m). Over this cornice there follows again a covered slope in which, in its lowermost portion, landslides of red areno-argillaceous rocks (about 20 m) are observed. Then, along the slope a new cornice is traceable composed of yellow, frequently oolitic limestones; locally passing to sandstones (7—10 m). This limestone seems to belong to the Alai stage. It should be noted that in this limestone the oyster fauna is absent. Generally speaking, it is a very strange phenomenon, since the oysters of the Alai stage present most widespread and persistent forms.

The Alai limestone is followed higher up by a considerable perfectly covered space (about 50 m thick), after which among reddish soddy slopes there appear beds of shell rock with an abundance of flat Rishtan oysters—*Ostrea (Platygena) asiatica* Rom. and of shells predominating in number, which represent a new species—*Platygena lada* sp. n. Shortly after begins an areno-conglomerate series, probably of the Bactrian stage.

Thus, the presence of the Rishtan stage in the marine facies has been established. *Platygena asiatica* Rom. is actually present here, but not in the horizon indi-

cated in literature. It seems that between the Alpine limestone and the Rishtan shell corks, deposits of the Turkestan stage are also developed; they are, however, hidden under the soddy slope. The section next southward is located on the right bank of the Gulcha River, 1 km upstream of the Kizyl-Kurgan. Here above the Danian gypsum a thick series of white cavernous limestones of the Bukhara stage is exposed, frequently breccia-like as a result of dolomitization (50 m).

The Suzak stage consists of two parts—a lower areno-argillaceous one, greenish-grey in colour; and an upper one, red-coloured and gypsiferous. The lowermost portion of this stage is concealed by a talus (about 10—15 m). This is followed by compact cavernous whitish-yellow; somewhat marlaceous sandstones forming an easily traceable crest (10 m). They are succeeded by green arenaceous clays and argillaceous sandstones; containing several bands of greenish-yellow marls with *Cardita* sp. (15 m).

The upper portion of the Suzak stage is represented by gypsum; alternating with red clays and sandstones; in rare cases bands of green clays are encountered. Thickness about 60 m. Over the Suzak layers a compact limestone of the Alai stage, with *Ostrea turkestanensis* Rom. (10 m); projects as an abrupt cornice.

In the very core of the syncline inclined towards the river, well delineated by Alai limestone, green clays are hardly exposed, over which, after a small reddish talus, there follows a bed of gypsum. The total thickness of this formation does not exceed 6—8 m. The higher horizons at this place are absent.

It should be emphasized that in this section the Suzak stage consists of two members. In Southern Ferghana the Suzak stage is represented by gypsum and red clays; *i. e.* by rocks analogous to those composing the upper part of this stage in the Kizyl-Kurgan section. On the contrary, in North-Eastern and Northern Ferghana the Suzak stage is represented by the marine facies and consists of green clays and partly of sandstones with a bed of oyster limestone with *Ostrea hemiglobosa* Rom. var. and *Gryphaea errara* Vial. (1). Closely similar to this facies is the lower part of the Suzak stage of the Kizyl-Kurgan section, in which a passage from the South- to the North-Ferghana type may be observed.

The third section examined is located south of the Sufi-Kurgan fortifications; near the mouth of Kunek-Sogdy, a right-hand side tributary of the Gulcha River.

1) Upon the pink sandstones and gypsum there rests a series of light-grey; greenish and yellowish limestones; sometimes marlaceous (15 m). They form a continuous cornice together with the covering gypsum, to which bands (20—40 cm) of white, yellowish finely porous limestones (10 m) are subordinate. The gypsum undoubtedly belongs to the Bukhara stage; to the same stage probably refer also the light sandstones.

2) The Suzak stage is represented by grey and pink loose sandstones (20—25 m).

3) Following higher up is a grey rubbly marlaceous limestone of the Alai stage with *Ostrea turkestanensis* Rom. et var. *alaica* Vial.; projecting in a crest (6—8 m). It is overlain by a grey compact sandstone (5 m), most probably belonging also to the Alai stage.

4) The Turkestan stage begins with loose greenish argillaceous sandstones, in which in the talus one specimen of *Fatina esterhazyi* Pav. has been found (35 m).

This series is crowned by light yellowish sandstones (8—10 m), forming a distinct cornice. Further on, a series of mainly greenish and grey sandstones is exposed; which are now loose and more or less argillaceous, and now compact, projecting as crests. In the upper part of this series valves of *Platygena asiatica* Rom. have been found, which are evidence of the presence of the Rishtan stage.

5) Somewhat uncertain is the position occupied by the lower strata of this series, referring either to the Turkestan or to the Rishtan stage: arenaceous gypsum (5 m) and greenish loose sandstones and arenaceous clays overlying the former, among which two crests of grey more compact sandstones (5 and 8—10 m) stand out. The whole series is crowned by similar compact grey sandstones (15—20 m). Its total thickness is about 65 m.

6) A doubtless Rishtan stage begins with massive or thick-bedded brick-red sandstones with a coarsely cellular surface of weathering. They give way to crimson

clays alternating with sandstones. This red-coloured series is prominent on the slopes as a bright persistent band. Its total thickness is 40 m. It is followed by loose greenish clayey sandstones (6—8 m), compact yellowish sandstones, forming a considerable projection (about 20 m), and then by a covered slope, probably composed of alternating bands of greenish-grey and red sands (40 m). They are overlain by dark-green pure clays (8 m), containing *Platygena asiatica* Rom. The latter give way to pink and to light greenish-grey sandstones, also with scarce *Platygena asiatica* Rom. (about 12 m).

7) To the Isfarin stage belongs only a thin (5 m) bed of pink sandstone.

8) The Khanabad stage is represented by greenish-grey marlaceous sandstones very thin- but uneven-bedded, with irregular cylindrical sandy concretions. These sandstones standing out in a sharp crest contain indeterminable remains of small costate *Ostrea* sp. and *Pecten* sp. In the roof they become reddish, and the quantity of the fauna, while remaining uniform, greatly increases; *Turritella* sp., *Pecten* sp., *Ostrea* ex gr. *flabellulaeformis* Schaur. have been determined here. Thickness 8 m.

9) Over the horizon with oysters begin red-coloured rocks. At the base lie brownish- or pinkish-grey sandstones with bands of green and grey ones; in the upper part of the series, distinguishable on the slopes as a whitish-pink band, there lies a gypsum bed, about 3 m thick. The thickness of the whole series is up to 15 m. The author refers it quite provisionally to the Khanabad stage.

10) The Sumsar stage, just as it is in most places, consists of crimson rocks. It may easily be subdivided into two parts. The lower one consists of alternating brick-red sandstones and crimson clays with bands of light-grey or nearly white loose sandstones (up to 30 cm). In the lowermost portion there is intercalation of yellow arenaceous marls. Thickness 10 m.

The upper part is mainly a clayey one. An alternation at frequent intervals of banded crimson clays with very finely schistose clayey sandstones and finely platy sandstones is observed here. Such riders (30—100 cm) are separated by beds of pink sandstone and gypsum up to 70 cm. The thickness of the total series is 40 — 50 m. It is clearly distinguishable on the slopes in a crimson band.

11) The Massaget stage begins with a 30 m thick series of brick-red sandstones and clays. In the lower part clays, and in the upper one, sandstones predominate, alternating with clays. Further, red beds of ungraded rubbly conglomerates (brecias) are developed. Of the higher horizons none has been examined.

In the section described one is struck in the first place by the unusual development of sandstones. Clays are of a quite subordinate importance, and carbonate rocks are nearly lacking altogether. It should be noted that the Cretaceous section, too, is of the same nature and consists mainly of sandstones. It is very interesting to emphasize the presence of *Platygena asiatica* Rom. As it is known, in the Tadjik depression this form is absent; it has been supposed that it does not occur in the Alai Range either, and that the statement in the literature concerning the finding of this species on the Gulcha ([5]) is based on some misunderstanding. It seemed that the marine facies of the Upper-Ferghana subdivision were not developed in the Alai Range. Now it may be affirmed that they are present here. The Khanabad and Sumsar stage have been established here for the first time.

In comparing the sections of the Trans-Alai Range (Bordoba), Alai system and Ferghana, after they have been reduced to a cumulative Central-Asia stratigraphical scheme, it may be easily noted that the southern Alai section (Kunek-Sogdy) is the most shallow-water one. Thus, in the region of Kunek-Sogdy the Ferghana and Tadjik Palaeogene basins were separated by a more shallow-water belt.

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MINERALOGY

DETERMINATION OF TEMPERATURES OF FORMATION OF HYDROTHERMAL MINERALS BY STUDYING LIQUID INCLUSIONS

By N. P. ERMAKOV

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In the first half of the last century the attention of a number of scientists was attracted by the presence of liquid inclusions in some minerals. The first to study them from the standpoint of composition was Dévy (1); who also established the presence of gas bubbles in the liquid inclusions. Brewster (2) was the first to observe these gas bubbles to disappear upon heating. In the middle of the last century Sorby (3) made the first attempts at a direct determination of the temperatures of formation of quartz crystals. Later on, Phillips (4) has noted that in the same quartz crystal the gas bubbles in the liquid inclusions would disappear at different temperatures. This phenomenon, confirmed at a latter date by a number of other scientists interested mainly in inclusions in quartz (5–7), discredited the view as to the possibility to use these inclusions for determining the temperature of formation of minerals.

In 1929 Laemmlein (8) proved beyond doubt that in the minerals there occur large numbers of secondary liquid inclusions with gas bubbles formed as a result of a dendritic mode of healing of fissures during the period subsequent to the crystals' formation.

In 1933 Newhouse applied the method of heating transparent laminae of cleiophane in a water bath placed on a microscope stage (10). The heating was carried on until the gas bubbles in the liquid inclusions disappeared, and this temperature, in his opinion, was characteristic of the moment of crystallization of the mineral from hydrothermae. In the opinion of a number of investigators, the cooling of the hydrothermal mineral and of the liquid inclusions within it brought about the separation in the latter of the gaseous phase in the form of a bubble, which is dissolved in the liquid after the temperature of formation has been restored (9). The experimental production of bubbles in the pores of transparent plastics, filled with heated water, —carried out by the present author, —enables us to assume that these bubbles are formed upon cooling mainly at the expense of a greater contraction of the liquid volume as compared to that of the enclosing rocks. The difference in the rate of reduction in the volume of the droplet of liquid enclosed and of the pore itself gives a vacuum filled with the vapour of the same liquid. It is natural that the more strongly heated was the mother hydrothermal liquor, the drops of which were entrapped and retained in the pores of the crystals by the new layers of matter built up, the larger would be the size of the gas (vapour) bubbles in the mineral. A heating of small pieces of plastics with artificial pores results in a destruction of the vapour bubbles produced at the temperatures of the water while filling these pores.

Under natural conditions, this phenomenon, however, is true only of low-temperature and weak solutions of the upper zone of mineral formation in which the concentrations and pressure cannot distort to any considerable extent the results of such temperature measurements.

The author, who was for several years carrying on a study of the deposit of optical minerals in Central Asia, following the advice of Prof. V. M. Kreuter used the method of heating the crystals, with the object of determining the temperature conditions of formation of these deposits representing the upper zone of hydrothermal formations ([11]). In the course of his study the author distinguished primary inclusions enclosing the mother hydrothermal solution, and secondary inclusions characteristic of the solutions which were at different periods healing the fissures in the crystals. In the former, the moment of disappearance of the gas bubbles would give some idea of the temperatures of the medium in which the crystallization and formation of the deposits were taking place; the secondary inclusions characterized the whole of the subsequent stage, sometimes up to the period of the deposit becoming exposed at the surface. The author was interested only in the first point; therefore, according to Laemmlein ([8]), he endeavoured by using a number of diagnostic features to separate out and study only authigene primary inclusions.

Jointly with P. V. Zybutschev, engineer-geologist, the author designed in the form of a small thermometer a device to be used with the binocular for heating crystals, changing their temperature and observing gas bubbles. The heating was made to proceed very slowly in order that the temperature of the thin lamina of the crystal would correspond to that of the surrounding air and of the air within the enclosed space, where beside the crystal the end of the mercury thermometer was placed. A control of the accuracy of the observations which were usually made on several bubbles was achieved by repeating the observations.

We have studied 140 crystals from 22 deposits of iceland spar, optical fluorite, optical baryte and rock crystal. From the Kulikolon deposit, from different pockets and veins, 60 crystals of fluorite, barite and calcite were studied. The disappearance of gas bubbles in the liquid inclusions of different barite crystals took place between 119 and 152° C; of fluorite, between 101 and 136° C; and of calcite, between 89 and 108° C. Thus, the mean arithmetic temperature of barite crystallization, which seems also the most characteristic of the Kulikolon deposit, is 138° C; that of fluorite crystallization, 122° C; and of calcite, 101° C. All the crystallization temperature measurements were found to be exactly corresponding to the sequence of the crystallization of minerals established at the deposit, with a lowering of the temperature of formation from barite through fluorite to calcite. In pocket No. 47 barite was crystallized at a temperature of 152° C; fluorite, at 135° C; and calcite, at 107° C. For each pocket one is struck by a constant temperature range, approximately 16°, between the crystallization of barite and fluorite.

It seems hardly probable that this persistent range of the crystallization temperature for numerous pockets far removed from one another is an accidental one; the causes of this phenomenon, however, are as yet not clear to the writer.

At the Middle Kaznok deposit measurements of optical fluorite and of fluorspar were made; they showed an average temperature of the disappearance of bubbles of 112° C. At the Aurakhmat deposit nine various-coloured fluorite crystals showed a temperature of crystallization within the range from 121 to 149° C. The most low-temperature one was found to be a pink semi-transparent fluorite; and the most high-temperature one, a deep-violet and a colourless fluorite. The crystals of optical barite from the Porvin deposit, occasionally containing small inclusions of cinnabar, showed a temperature of the disappearance of the bubbles of 69 to 91° C. A barite crystal with inclusions of fahlerz from the Maghian deposit showed a temperature of 98° C; and a barite from the Marguzor deposit with radial inclusions of antimonite, 126° C. The average crystallization temperature for eleven deposits of iceland spar, occurring in Palaeozoic limestones, has been found to be 79—80° C. However, under quite different geological conditions, the formation of calcite seems to be possible at considerably more elevated temperatures. Thus, a transparent calcite from the skarns of Chatkala and Pskema (Akbulak) showed tempera-

tures of disappearance of bubbles of 195 and 275° C. Rock crystal formed within a very wide temperature range, owing to an extensive development of secondary inclusions, required particular care in temperature investigations. Only the most reliable measurement of the temperature of disappearance of bubbles in piezoquartz from the Pamir deposits will be cited, namely: Lyangar, 82—83° C; Barnavadge. 158—160° C; Pasthuf, 216—220° C.

The use of a direct method for the determination of the temperature of crystallization for low-temperature hydrothermal optical minerals from the deposits of Central Asia was in no case of a joint occurrence in some pocket or other in conflict with the paragenesis and sequence of crystallization of these minerals. The joint occurrence in the same crystal of several groups of bubbles disappearing at different moments upon heating does not invalidate the method, provided the primary liquid inclusions are correctly distinguished from the secondary ones.

The proposed method for studying liquid inclusions should find wide application to the study of the temperature of formation of many ore and non-ore low-temperature hydrothermal deposits, since both transparent and semi-transparent minerals with liquid inclusions and bubbles of gas occur rather frequently. These inclusions are also a good objective criterion in distinguishing cold-water minerals from hydrothermal ones; and the latter, from pneumatolitic ones.

The possibility of determining the temperature of crystallization, in addition to theoretical interest, must have a practical value in the industry for the production of artificial crystals of some mineral or other, and for evaluating the quality of the crystals as a raw material mined from deposits of piezo- and optical minerals.

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PALAEONTOLOGY

ON THE ANCIENT CALCAREOUS ALGAE OF THE TIMAN RIDGE

By A. G. VOLOGDIN, Corresponding Member of the Academy

The first to discover calcareous algae in the old carbonate rocks of the Timan Ridge has been K. K. Wollosovich. The first findings have been made a few years ago in the south Timan Ridge in the beds of the Ropcha series, along the Pot-Yu River.

In 1940 Mrs Kalberg, geologist, discovered algae in the Middle Timan Ridge (Chetlassky Kamen), along the Svetlaya River (the first lateral valley on the right-hand side in the upper course of the river) and the Bystrukha River. Both the first and the new findings of algae point to the important part taken by calcareous algae in the formation of the carbonate rocks of the old Timan series, which are assigned by some authors to the pre-Cambrian, and by others, to the Early Palaeozoic. Unfortunately, the examination of the algae collected showed them to be poorly distinguishable because of the considerable degree of metamorphism. The latter is expressed in the finely crystalline structure of the algal limestones, the microstructure of the algae having been almost completely obliterated. Some specimens, *e. g.* from the Svetlaya River, were found to contain accumulations of bitumens, subordinate to some of the stromatolite strata and therefore clearly emphasizing their stratified structure, in spite of a strong recrystallization of the rock.

As the modern study of stromatolites is mainly based upon mictrostructure, the above specimens of algae remain as yet undetermined. From the macrostructure, however, it may still be said that it has been possible to distinguish within the specimens forms of the type of *Collenia* Walc., characterized by a columnar structure of the thallus and making up the whole of the given rocks. The diameter of the columns is from 2.0 to 4.0 cm. The thallus are smooth; continuous; protruding upwards by $^1/_3$ of the cross-section. Similar forms are found also in the Lower and Middle Cambrian of the Siberian platform.

In one specimen from the Bystraya River areas of limestones are distinguishable; which are composed wholly by small bodies that may be assigned only to the algae of the poorly studied onkolith group (*Onkolithi* Pia). The age significance of this finding is as yet uncertain.

Thus, this new palaeontological material may be taken to be evidence in favour of a Lower Palaeozoic age of the metamorphic series of the Timan Ridge (not higher than the Lower Silurian), and of a platform nature of the algal facies, a direct analogy with the Lower Palaeozoic of the Siberian platform being observed. As each of the specimens studied is found to contain new algal formations, it is evident that the section of the metamorphic series of the Timan Ridge is very rich in these remains, playing here an important part in the formation of rocks. It may be noted that after sufficient amounts of this material will have been collected, we shall be able to correlate it with the ancient algae in a more reliable manner and thus arrive at a final solution of the important problem as to the age of the oldest beds of the Timan Ridge.

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GENETICS

WAYS OF STABILIZATION OF GENOTYPE

I. SELECTION OF STABLE ALLELOMORPHS

By M. V. IGNATIEV and N. I. SHAPIRO

(Communicated by L. A. Orbeli, Member of the Academy, 29. III. 1944)

The analysis of the mutation process; as viewed under its historical aspect, has shown that the regularities in the arising of mutations now observed are a result of a long evolution (1).

On the basis of some *a priori* considerations, as well as of evidence available, the conclusion has been arrived at that the evolution of mutability proceeds from its highest rate to the minimum. Until the present time no detailed theoretical analysis has been suggested of the possible ways of the stabilization of the genotype; or of the selection of the most stable hereditary structures. All that is known is that the selection of stable genotypes may proceed along two lines simultaneously: 1) by way of selection of stable allels and 2) by way of selection of special genes — mutability modifiers.

The present note contains a summary of a genetical-mathematical analysis of the question as to the possibility and the ways of the selection of the most stable allels within a population.

The authors have considered cases where the allels differed as to the rate of mutation into a lethal; in other words, to such an allel as reduces the chances of a mutant individual to produce progeny. Such cases have also been analysed where the allels differing as to their rate of mutation have equal chances to mutate into a lethal, or in other words, there is absolutely no mutation in this direction. Let us assume that the mutant gene is recessive and that it is located in the autosome.

The conditions specified above are chosen because of their frequent occurrence under natural conditions. The conclusions arrived at can, however, be extended to some other cases as well (say, to the intermediate mutant gene, *etc.*).

1. If a population contains two normal allels of the same gene, differing but by the rate of mutation towards a recessive lethal, and if there are no reverse mutations between the normal allels, the labile gene should theoretically be entirely substituted by the more stable one.

2. In the case where reverse mutations take place between the two competing allels, no total supplanting of the labile gene by the more stable one is likely to take place.

3. In the case of exchange mutation, the concentration of the stable and of the labile allels tends towards equilibrium. This equilibrium depends on the correlation between the frequencies of exchange mutations between the allels and the rate of mutation of the normal allels into recessive lethals; it may be expressed by the formula

$$\frac{p}{q} = \sqrt{\frac{v''}{v'} \frac{u'' + v'' - p^2}{u' + v' - p^2}}$$

where p, q and r are the concentrations of the labile and stable allels and of the recessive lethal; respectively; u' and u'', the rates of mutation of the more labile and more stable allel into a lethal; and v' and v'', analogous rates of exchange mutations.

4. If the correlation between the mutation rates of the normal allels and the lethal is equal to the rates of the exchange mutations; or if the rate of exchange mutations is higher; then the concentration of normal allels will be approximately inversely proportional to their rate of mutation.

5. If the rates of mutation of each of the allels in different directions are disproportional, two cases may be differentiated: a) either the rate of exchange mutations is higher than that of the mutation into the recessive lethal; the equilibrial concentrations do then somewhat diverge from the inverse proportionality with the rate of mutation; d) or else, the rate of exchange mutations is lower than of mutation towards the recessive lethal.

In this case the labile gene tends to be almost entirely excluded by the more stable one.

6. If a large number of allels is present; each of which has a rate of mutation towards the lethal of its own (which is the only distinctive feature of these allels), then the equilibrium cannot be established unless the mean mutation rate of the series as a whole (more strictly speaking, the mean of the mutation rates of the series of allels) has been reduced to a low level. The height of this level should not much exceed the mutation rate of the most stable allel. The distribution of the allels is, moreover, inversely proportional to their mutation rates (in other words, a hyperbolic distribution is obtained).

7. The hyperbolic distribution also takes place if recessive lethals are lacking (or if all of the allels mutate towards the lethal at an equal rate).

8. In agreement with the character of hyperobolic distribution of a series of allels differing by their rate of mutation alone, the most frequently recurring are the most stable allels. This mode of distribution secures, however, a sufficiently high dispersion of the rates of mutation.

Owing to this, allels with a high mutation rate are necessarily maintained in the population.

9. Stable allels which have an insignificant selective advantage are subject to the danger of fortuitous extinction. In order that such a newly arising gene receive further distribution, it is necessary that it reach in the same occasional way a definite frequency. The probability of its attaining a necessary level in the case of recurrent mutations becomes a high one within a relatively short period of time.

10. The rate of establishment of limit concentrations of the labile and stable allels depends on a number of circumstances; and in the first line on the value of the difference in the rate of mutation of the different competing allels.

11. The increase in the mutation rate from a labile allel towards a stable one shortens markedly the time within which the latter conquers the population. The relation between the number of a fully stable gene and the number of generations from the moment where the gene started to profit of its advantage; may be expressed by the formula:

$$q_t = \frac{e^{2ut} - 1}{e^{2ut} + 1}$$

where q is the concentration of the stable allel; u, the rate of mutation of the labile gene in either direction; t, the number of generations that succeeded one another since the moment the mutant gene had started its «conquest» of the population.

12. The rate at which limit concentrations are attained by the two competing allels, at the condition of mutual exchange mutations and of an absence of lethal mutations, may be expressed by the formula

$$q_t = \frac{v'}{v' + v''} [1 - e^{-(v' + v'')t}]$$

where q is the concentration of the allels whose mutation rate is equal to v'. In this case the process goes on more slowly than in the case where the allels differ as to their rate of mutation towards a recessive lethal.

13. The above equations of distribution of stable allels hold good for the mean values of concentration during a given generation. In separate cases both slower and more rapid propagation may occasionally take place, since the number of mutations within any generation is subject to considerable dispersion.

14. If a series comprises numerous allels each of which displays a peculiar mutation rate of its own (which is their only point of distinction), then the rate at which they approach equilibrium is dependent on their original distribution. And the more the allels differ in their mutation rate, the higher will be the rate of the process.

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PLANT PHYSIOLOGY

A CONTRIBUTION TO THE PROBLEM OF RUBBER FORMATION IN THE ROOTS OF KOK-SAGHYZ

By P. S. BELIKOV

(Communicated by A. A. Richter, Member of the Academy, 16. II. 1944)

The root-rubber plants are not high in rubber. Recalculated to raw weight the rubber content in kok-saghyz, tau-saghyz and krym-saghyz attains during the first year of cultivation 2—3, 1—1.5 and 0.4—0.5 per cent, respectively. It is but natural therefore that from the very first steps of the cultivation of those rubber-plants attempts have been made by various investigators to find out such conditions as would stimulate the formation of rubber in them. Mazanko (3) has demonstrated that the store of latex is continuously renewed in the laticiferous vessels, which made it possible to develop the method of tapping and thus twice to increase the output of rubber from a plantation (4). It remained obscure, however, whether rubber is being formed anew in the evacuated laticiferous vessels; or its migration takes place from the lower portions of the rootlets, for the experiments were carried out with tau-saghyz root left in the ground.

It is not until recently that direct evidence has been secured (5), pointing to the possibility of the formation of rubber in kok-saghyz roots at the expense of the mobilization of plastic substances. It has been demonstrated that roots of kok-saghyz, severed from leaves and isolated from soil (stored in heaps), are able to accumulate rubber; losing at the same time a considerable part of polysaccharides.

It is a matter for regret that the author of this highly interesting and important work, who has been the first to observe that the roots become higher in rubber during storage, has left out of the scope of his investigation the relation between the enrichment of roots with rubber and the conditions of storage. A thorough knowledge of such conditions as are favourable for the formation of rubber would be of paramount importance, however, enabling the rubber-plant breeder to control this process.

The present work was carried on in 1943, at the Mikhnevo experiment field of the Rubber-Plant Institute. During the spring were investigated the roots of kok-saghyz planted in the spring of 1942, during summer and autumn, those of the 1943 planting. The day previous to the experiment the roots of kok-saghyz were dug out, scrupulously cleansed and washed, severed from the leaf-rosettes at the level of the root crown, after which they were divided into separate lots assorted according to length and shape. Axial roots only were taken for experiment. The roots sorted out and prepared in this way were wrapped in wet cloth and left until the next day.

The fixation of roots was done with hot vapour during 15 minutes, by keeping them in a closed pail of boiling watter. The roots were reduced to air-dry condition

in an exsiccator, at a temperature of 50—60° C. The content of rubber was determined by the extraction method in experiment No. 3; and by the alkali method, in the rest of experiments (1).

The following assumption has been laid by us at the basis of our experiments. If we were to assume that considerable amounts of rubber can be formed in the laticiferous vessels even after the roots are severed from the leaves and isolated from the ground; *i. e.* without any mineral or aerial nutrition, only at the expense of polysaccharides and of their subsequent synthesis into rubber, then by periodically extracting the rubber from the laticiferous vessels, by evacuating them, it must be possible to bring about synthesis again. In agreement with this assumption the following conditions were to be established: 1) the roots should be wilted; as an indirect means to enrich them with monosugars; 2) the laticiferous vessels should be evacuated by extracting from them the latex and rubber contained.

The roots were wilted during some 24 hours at room temperature, and cut from above into slices 2—3 mm thick; we proceeded in cutting until the surface of the sections was found to be covered with latex, then cutting was reassumed after 2—3 days.

Experiment No. 1. Started on September 10; ended on October 6. Temperature during experiment; 12—15° C. Wilting of roots during 2 days. Within this time they lost 11—12 per cent of their initial weight. In the subsequent the roots were kept under conditions similar to those of the controls; *viz.* wrapped in wet cloths. The results of the experiments are given in Table 1.

Table 1

Kok-Saghyz Roots Enriched with Rubber by Means of Wilting

No. of set	No. of replication	Procedure	Rubber content per raw weight, in %		Increment or loss in rubber as compared to control, in %
			per replication	average	
1	1	Control, root fixation at the beginning of experiment	2.70	2.65	—
	2		2.61		
2	1	Kept during 26 days in a humid chamber	2.64	2.65	0
	2		2.65		
3	1	Wilted during 2 days at 14—15°, kept for 24 days in a humid chamber	3.27	3.22	+21.5
	2		3.16		
4	1	Same as in set 2, save for cutting done on 10 and 12.IX	2.47	2.45	—7.5
	2		2.43		
5	1	Same as in set 3, save for cutting done on 10 and 12.IX	2.86	2.88	+8.7
	2		2.90		

The results of this experiment give ground for the following conclusions: 1) Roots kept during a long period of time in a humid chamber; preventing the roots from losses of moisture, display no alterations in their rubber content.

2) When wilted; the roots are found to have increased in rubber.

3) If cutting is done under conditions of air dryness; a loss in rubber is observed (experimental sets 2 and 4; 3 and 5).

Analogous results have been obtained with an experiment carried out during 24 hours. It is of interest to compare them with the data available in literature. Lebedeva (2) has carried out an experiment which demonstrates that in the case of wilting the increase of the plant in rubber is both a relative and an absolute one. Although in her experiment she has been dealing with plants not deprived of their leaves; the results secured have, however, bearing on the problem here discussed. The experiments compared are based upon the same phenomenon; *viz.* on the direct influence of root wilting upon the formation of rubber in them. Experiment No. 1 went to confirm the assumption made by us as regards the effect of wilting, yielding unexpected results in the set involving the cutting of roots;

instead of a rubber increase; loss of rubber has been observed in this set. A whole series of new tests has been found necessary in order to check up the correctness of the experimental data. Part of them will be described in what follows.

Experiment No. 2. The purpose of the experiment has been to determine the influence of the replication of cutting upon the contents of rubber in the roots of kok-saghyz.

The experiment was started on August 26, ended on September 13. The roots of all sets were kept in a humid chamber. During the experiment the temperature ranged between 15—20° C. The results are given in Table 2.

Table 2

Loss of Rubber by Kok-Saghyz Roots as Dependent on Replication of Cutting

No. of set	No. of replication	Procedure	Rubber content per raw weight, in %		Increment or loss in rubber as compared to control, in %
			per replication	average	
1	1	Control, fixation of roots			
	2	at the start of experiment	2.20	2.15	—
			2.10		
2	1		2.29	2.19	+1.8
	2	No cutting	2.09		
3	1		1.92	2.00	—7.0
	2	Cutting done once	2.07		
4	1		1.79	1.85	—13.8
	2	Cutting done twice	1.92		
5	1		1.75	1.68	—21.8
	2	Cutting done three times	1.60		
6	1		1.50		
	2	Cutting done four times	1.67	1.58	—26.5
7	1		1.42		
	2	Cutting done five times	1.50	1.46	—32.1
8	1		1.92		
	2	Cutting done six times	1.85	1.88	—12.1

From Table 2 it is evident that the larger the number of cuttings made; in other words; the larger the amount of latex put in contact with air; the smaller is the content of rubber observed. An exception to this rule is offered; however, by the roots in experimental set No. 8; where the amount of rubber exceeds that of the preceding set; being lower than in the control. Repeated cutting results in a dehydration of the root. Two processes are operative here: the one (wilting) bringing about an increase in rubber content; and another (cutting) which goes to reduce it.

The phenomenon observed seems to be due to the fact that being deprived of the protective tissue of the root or of any other substances protecting the rubber from oxidation until it is kept in a close system, *viz.* in the laticiferous vessel; the rubber undergoes oxidation. In order to check up this conclusion; the experiments have been reproduced in an atmosphere deprived of air oxygen. A preliminary experiment; run under conditions of impeded rubber oxidation; gave positive results.

Experiment No. 3. The specific conditions of this experiment consisted in that the roots tested were kept in exsiccators over a layer of water. These conditions stimulated a rapid oxygen consumption by roots on respiration; and its replacement by carbon dioxide. The exsiccator; of a 4 l capacity, could be made to hold up to 300 g of roots. According to observations made by Prof. Oparin; the roots of kok-saghyz evolve about 1 mg of carbon dioxide to 1 g of dry weight per hour. Within 24 hours scarcely any oxygen was left in the exsiccator. Under these conditions the aeration of the roots was impeded.

The experiment was started on April 2, ended on April 29. The temperature during the experiment varied within 12—16° C. The results are summarized in Table 3.

Table 3

Kok-Saghyz Roots Enriched with Rubber by Cutting them at Regular Intervals under Conditions of Hindered Gas-Exchange

No. of set	Procedure	Rubber content per raw weight in %	Rubber increment compared to control, in %
1	Control	1.26	—
2	Kept during 8 days under conditions of hindered gaseous exchange, without cutting	1.37	+8.7
3	Same; cutting done 4 times	1.88	+49.1

The results of this experiment are in contrast with those of the preceding one. This time the cutting of the roots; instead of reducing the content of rubber; has resulted in an increase in rubber, which was rather considerable; nearly by 50 per cent as compared to the control. This result should be put down; as pointed out above, to the conditions of impeded gaseous exchange.

The study we have undertaken is the first attempt to penetrate into one of the most fascinating domains of modern physiology; *viz.* that of rubber formation. According to the actual information on the subject ([6]), the synthesis of rubber proceeds within the laticiferous vessels; it may take place without any direct participation of either aerial or mineral nutrition. Owing to this; experiments carried on with roots dug out of the ground and severed from the leaves offer; aside from their high practical interest; a number of methodical advantages, as well. It is necessary to subject to a manysided study the transformation of substances in the roots of rubber-plants, in the first line this refers to the sugars which are most likely to be the predecessors of rubber in the process of synthesis.

Conclusions. 1) Under conditions of constant humidity of the roots. the content of rubber in them also remains constant, 2) the wilting of roots is accompanied by an increase in their rubber content; 3) if the roots are subjected to surgical treatment under conditions of good aeration, there is a decrease in their rubber content; the latter being the more intense, the larger the amount of latex lost by the laticiferous vessels during the operation; 4) under conditions of hindered gaseous exchange the roots are enriched with rubber.

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PLANT PHYSIOLOGY

CONDITIONS OF FORMATION, DEVELOPMENT AND DIFFERENTIATION OF A CALLUS

By W. O. TAUSSON

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The root cuttings of our native rubber-plants; the krym-, kok- and tau-saghyz, are well known for the extreme ease with which they form leaves; their ability for root regeneration is, however, a very poor one (1). It has been reported, moreover, that both their increase in the ability of forming leaves and the decrease in the ability of forming roots are the more expressed; the higher the given plant is in rubber. The application of such growth-substances as the heteroauxine goes markedly to change this relation (1); it does not fully eliminate; however, all the difficulties involved in the propagation of root-rubber plants by cuttings, which is especially true for tau-saghyz. All that has been said here makes it necessary to study in detail all the conditions of the formation, development and differentiation of the callus (which is produced from cambium in the case of cutting).

Without denying the important rôle of auxines in the morphogenetic processes (2, 3), we must not underestimate the part played in these processes by the synthetic activity of the cells of the tissues, especially of the embryonic ones, for this part is by no means a lesser, and possibly even a more essential one. The development and growth of separate tissues and of entire organs is invariably and necessarily connected with the formation anew of the most various cellular substances. The course, the trend and the intensity of the processes of their synthesis by live cells cannot therefore otherwise than essentially affect, sometimes even in a decisive manner, the nature and relative intensity of the development of the tissues and organs that are formed anew.

From the fundamental principles of the author's theory of the exothermic nature of biological syntheses (4) it should be inferred that the course, direction and ultimate results of the synthetic processes that take place in living cells are largely determined and controlled by the conditions of gaseous exchange. Indeed, according to this theory, the synthesis from carbohydrates of such substances as the aminoacids, fatty acids *etc.* whose carbon chains are mainly built of methyl and methylene groups, is stimulated by a somewhat reduced supply of oxygen. In contrast with this, polysaccharides of the type of cellulose are more readily formed from simple sugars under conditions of a liberal aeration. These correlations are in good agreement with the fact that free oxygen has more than once been reported to produce an inhibiting effect upon the reaction of the splitting of hexoses into trioses («triosis») (5). It seemed therefore very probable that the conditions of gaseous exchange must affect also the course and the trend of

form building processes; in particular; the formation, development and differentiation of a callus.

When attacking the problem in an experimental way, the following two statements served us as points of departure:

1) The growth and development of a meristematic tissue is accompanied by an increased synthesis of the live contents of the cells, mainly of proteins, and by a relatively weak and slow formation anew of the components of the cellular membrane, especially of the cellulose; which is favoured by a rather reduced gaseous exchange. Unlike this, the differentiation of tissues is connected with a considerable decrease in the intensity of formation of the components of the protoplasm and with an increased synthesis of those substances which make up the wall of the cell; this process is stimulated by the conditions of high aeration.

2) A callus should be considered as an independent structure (an organism), developing on (or parasitic of) a cutting which serves for the callus as a living substratum.

In all the experiments carried out in the course of this investigation it was only the callus that was subjected to the effect of various regimes of gaseous exchange; while care was always taken to keep the cuttings themselves under optimal conditions for preserving and maintaining their life activity. The experiments described below were carried out in the dark and at a temperature of about 14—20° C.

The experiments carried out with the aim to investigate the influence of gaseous exchange upon the formation of a callus from cambium were based upon the fact that the cutting of roots is invariably leading to the formation at the surface of the sections of calluses which in the subsequent give rise to the formation of leaves. On the other hand, the operation undoubtedly results also in a sharp change of the tissues adjoining the point of the cut; *viz.* in an increase of the gaseous exchange. This phenomenon is evidenced by a rather rapid alteration of the colour at the surface of the section; which passes from a light-yellow to a pink; reddish, violet and ultimately to a red-brown and dark-brown; probably owing to an increased work of polyphenol-oxidase (6). The existence of a direct and intimate connexion between the two phenomena seemed to us highly probable and even indubitable.

Numerous experiments; involving partial or absolute elimination of any sharp change in the gaseous exchange in the case of cutting, were carried on with roots of two-year-old tau- and krym-saghyz plants; the surface of the cuts was sealed with glass, cork, celophane, paraffin, wax, fresh latex from a corresponding rubber plant, *etc.*; or else by immersing them in water directly upon cutting. The procedures listed above have been found, by hindering to a various degree the increase of gaseous exchange, to slow down or even fully to prevent the formation of a callus at the surface of the cut.

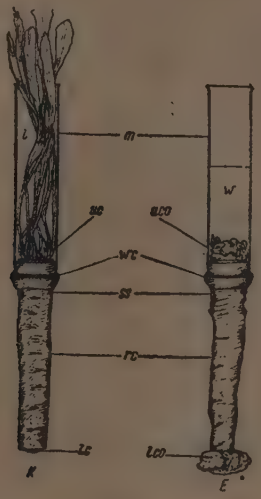
Experiments with the roots of one- and two-year-old plants of krym-saghyz, made with the purpose to increase the gaseous exchange in the root cambium by partly removing the surrounding tissues (bark and basic parenchyme); invariably revealed a different picture: the development of callus was now accompanied by its differentiation into leaves all along the sections laid bare.

The experiments with the purpose to study the effect of gaseous exchange upon the development and differentiation of the callus were carried out with roots of one- and two-year-old krym-saghyz plants. The method was the same as described above, save for some insignificant modifications introduced according to the run.

Root cuttings 8 cm long were kept in moist sand in a horizontal position during 6—8 days, until at their morphological tops and bases there appeared well shaped «upper» and «lower» calluses, respectively, showing no signs of differentiating. Hereupon the upper ends of the cuttings were tightly fitted within segments of glass-tubes open at either tip and whose diameter somewhat exceeded that of the root; the tubes were fixed with soft wax (see figure). The root cuttings with their upper ends fitted in the glass-tubes were mostly planted in a vertical position into moist sand to such a depth as to leave the wax-coating uncovered. In some

of the cases the lower ends of the cuttings were immersed in water so that the larger part of the cutting remained exposed to the air.

The reduction of gas-exchange intensity was brought about by filling the glass-tube with water; the thickness of the layer of water varied as to experiment; ranging from 3 to 40 mm. As controls served cuttings whose glass-tubes were not filled



Development of callus as affected by gas exchange (scheme, $^1/_2$ natural size). *m*, glass-tubes; *wc*, wax coating; *ss*, surface of moist sand; *rc*, root cuttings. *K*, control: normal gas-exchange of a callus (glass-tube contains no water); *up*, upper callus differentiating into leaves (*l*); *lc*, lower callus arrested in its development. *E*, experiment: gas-exchange of the callus reduced by a 40 mm water layer (*w*) in the glass-tube; *uco*, upper callus grown without differentiation into a tumour-like structure; *lco*, lower callus grown without differentiation into a typical tumour

with water, and which consequently enjoyed a normal (non reduced) gaseous exchange. The latter could likewise be reduced by merely immersing the callus in water, but this procedure proved less suitable in our case.

The results of the numerous experiments, some of which lasted 1.5 months and even more, were found to be in fair agreement with one another: in those cases where the gaseous exchange was reduced, the callus was found to maintain its meristematic activity during a considerable period of time, and grew without differentiating into a tumour-like structure. Unlike this, in all cases of normal (non reduced) gaseous exchange there was a rapid ahd intense differentiation of the callus into leaves. The figure goes well to illustrate this observation.

The same method has been applied to the experiments carried out with the purpose to investigate the effect of the various regimes of gas exchange both upon the «upper» callus at different stages of differentiation into leaves, and upon the «lower» callus by inducing the latter to differentiate into roots, too. These experiments went to confirm and to supplement the results of the tests described at the beginning of this note. Without dwelling on them in any detail; let us shortly formulate the main results of the study; which are fully concordant with the fundamental principles of the theory of «exothermic biosyntheses».

1. The formation and further differentiation of a callus from cambium requires a gaseous exchange more intense than that which proceeds in a normal; intact root. The cutting of the root; resulting in a local increase of the gas exchange, stimulates therefore the development of a callus at the points of incision.

2. In the case of a maximum gas-exchange intensity; *i. e.* under conditions of liberal aeration, a differentiation of the developing callus into leaves is soon setting in; the growth of the callus itself is thereby considerably slowed down; and further on arrested altogether.

3. In the case of a gas-exchange intensity intermediate between the one characterizing an intact root; and that taking place if there is a free oxygen supply to an unprotected cambium and callus, the latter preserves its meristematic activity during an indefinite period of time, and grows without any differentiation; forming tumour-like structures.

4. In the case of a reduced gas-exchange in a callus at various stages of its early differentiation; it undergoes but partial differentiation; giving rise; along with tumour-like structures; also to leaf-like or scale-like malformations.

5. The tumours which develop from a callus under conditions of a reduced gaseous exchange are of the nature of malignant growth; for they preserve during an indefinite period of time such properties as are characteristic of embryonic tissues.

6. The differentiation of the callus into roots is also greatly dependent upon the conditions of the gaseous exchange which in this case is essentially different both by its nature and intensity from that which brings about a lengthy preservation by the callus of its meristematic activity, or its differentiation into leaves.

The experiments described in this note have thus revealed a direct and intimate relation existing between the formation, development and differentiation of a callus and the conditions of gaseous exchange; it has been found, moreover, that the processes referred to above can be controlled by duly modifying these conditions.

The results obtained go to confirm a number of theoretical statements ensuing from the theory of «exothermic nature of biological syntheses».

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PHYSIOLOGY

SENSIBILIZATION PHENOMENA IN COLOUR VISION

By L. A. SCHWARZ

(Communicated by L. A. Orbeli, Member of the Academy, 29. III. 1944)

In the course of earlier work the author has become aware of the fact that the value of the colour threshold of central vision may sometimes be reduced appreciably if the eye had been shortly before stimulated by some other colour. It is this phenomenon that has been the subject of the experimental study communicated below.

Method. The minimum brightness necessary to the observer in order to perceive chromatic colour was determined with a monochromator; by shifting the neutral photowedge placed in front of the collimator slit. The field of vision of the apparatus was a circle about 1.4° in diameter. The threshold determinations were performed by the extinction method (vanishing of chromaticity). A reciprocal value of the transparency of the corresponding part of the wedge was taken to be the relative measure of the eye's sensitivity to the given colour stimulus. Having determined in this way the initial sensitivity level («background») always put at 100, we proceeded to the determination of sensitivity to a definite colour whose sensibilizing effect was to be tested in the given experiment; this part of the experiment lasted 2 minutes.

After this the level of sensitivity to the first («background») colour was determined again; at 1; 10, 20, 30 and 40 minutes intervals. Eight observers were tested in this way for their sensitivity to monochromatic colours corresponding to 695; 610, 568; 515; 455 and 437 mμ.

Results. In the first line it has been found that a mutual sensibilizing effect is produced by the groups of complementary colours alone (red — green; yellow—blue). The other colours of the spectrum produce no sensibilizing effect with respect to one another. Thus; after an exposure to the red colour (610 mμ) the sensitivity to the green colour (515 mμ) has been found to increase more than twice; the sensitivity to the red has been found to increase nearly twice after the observer's eye has been exposed to the green colour.

The blue; yellow and violet have been found to produce no effect upon the sensitivity either to red or green.

On the other hand, the sensitivity to the blue colour increased three times after an exposure to yellow; and more than twice in the reverse case; while neither green and red; nor violet have been found to produce any effect upon the sensitivity to blue or yellow (Fig. 1).

It should be pointed out that the sensibilization which becomes noticeable since the first minute (no earlier stages of sensitivity could be possibly measured because of the experimental conditions) is gradually increasing; attaining its maximum towards the 20—30th minute.

In the first experimental run the initial sensibilization corresponded to a level of sensitivity equal to that of the usual state of the person under test. It seemed equally interesting and important, however; to follow up the behaviour of the chromatic thresholds under hypodynamic conditions; as well; for example; the observer was invited to throw back his head; which invariably produced a decrease in the

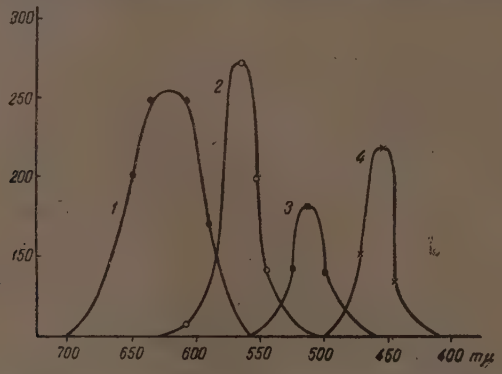

Fig. 1. Along the axis of ordinates is plotted (in per cent) the sensitivity recorded by the 30th minute after the sensibilizing action of the light stimulus has been removed; along the axis of abscissae is plotted the wave-length of the sensibilizing light, in mμ. *1*, eye sensitivity to the green colour (515 *m*μ). *2*, sensitivity to the blue (455 *m*μ). *3*, sensitivity to the red (610 *m*μ) 4. sensitivity to the yellow (568 mμ)

sensitivity of both hearing and nocturnal vision; or else; the observer was subjected to the effect of sensibilizing agents,say, of cold and other stimuli.

The sensitivity to both green and blue has been found to decrease strongly in such a state; while the level of sensitivity to red and yellow remained unaffected (Table 1).

Table 1

Effect of Hypodynamic State (due to head thrown back) on Colour Sensitivity («background sensitivity» put at 100%)

Wave-length in mμ	Colour	30′	60′	90′
515	Green	36	30	26
610	Red	99	100	110
455	Blue	44	31	30
568	Yellow	101	105	106

When the colour sensitivity reduced to a state of hypodynamics was exposed to the action of cold and colour stimuli; a single application of the former has been found to increase the sensitivity of the eye to the green colour 1.5 times as compared to the background level; and to makes it its double; if applied twice. Unlike this; the sensitivity to the red remained in the state of hypodynamics. Neither did it respond to the preliminary exposures to the complementary colour.

In spite of the phenomenon of selective mutual sensibilization within the groups of complementary colours observed at the beginning of these experiments, in the 2nd and 3rd runs the sensitivity to the red colour has been found to be different from that to the green; the same has been found to hold for yellow and blue.

Some experiments of Kravkov ([1]; [2]) and his coworkers ([3]) have clearly borne out the existence of an antagonistic relation between the green- and the red-perceiving apparatus.

The author feels inclined to believe that the relation existing between the sensitivity to the complementary colours is not only an antagonistic; but a much more complex one. If they showed in all cases nothing else than a mere antagonism, then under conditions of hypodynamics the sensitivity to the green colour would be invariably found to decrease; while that to the red would correspondingly in-

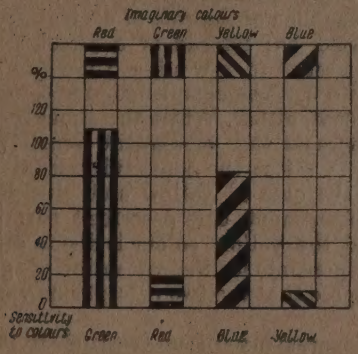

Fig. 2. Along the axis of ordinates is plotted the sensitivity increase observed by the 30th minute after the observer had been invited to awake in his imagination the colour specified by the experimenter.

crease. As a matter of fact; the sensitivity to red is found in such cases to remain almost constant. A similar picture is observable under conditions of sensibilization in the state of hypodynamics: the sensitivity to the red colour does not change here either.

Hence it may be concluded that the red and the green (as well as the yellow and the blue; correspondingly) are not equivalent to each other.

In order to shed revealing light upon this phenomenon; we have carried out a 4th run of experiments. Now sensibilization was achieved by means of a stimulus which was alternately applied either to the eye whose sensitivity level had previously been measured; or to the other eye. It has been found that the pre-stimulation with the red colour went to increase the sensitivity of the eye to the green; irrespective of the eye to which it had been applied, unlike this, no sensibilization to the red colour by means of a pre-stimulation with the green could be produced under our experimental conditions; unless the stimulus was applied to the eye to be tested (Table 2).

Table 2

Relation between Subsequent Colour Sensitivity of the Eye and the Effect of Colour Stimulus as Applied to the Eye under Test or to the other Eye («background sensitivity» put at 100%)

	Colour stimulus	Background colour	Colour sensitivity			
			1′	10′	20′	30′
Eye under test	Red	Green	212	217	242	249
Other eye	»	»	177	186	173	196
Eye under test	Green	Red	146	179	188	188
Other eye	»	»	95	98	100	100
Eye under test	Yellow	Blue	278	302	293	272
Other eye	»	»	140	162	193	190
Eye under test	Blue	Yellow	163	169	235	221
Other eye	»	»	100	101	99	99

In the case where the sensibilizing colour is applied to the other eye, the process involves higher located parts of the nervous system than in the case the stimulus is applied to the eye to be tested.

If we were to assume that the physiological levels of colour sensitivity are not the same for red, yellow, green and blue, this should certainly tell upon more complicate processes of colour perception, as well.

In order to gain a clear idea of the rôle of central processes, a special experimental run has been carried on; instead of a direct sensibilization by a light stimulus the observer was asked to awake the respective colour in his imagination. The complementary colours have not been found to be equivalent in this case, either. While the «imaginary» red colour has been found almost twice to increase the subsequent sensitivity to the green, the imaginary» green failed to affect the sensitivity level to the red.

The same holds for the case of yellow and blue (Fig. 2).

The results of the experiments here described permit us to assume that the perception of the red and the yellow colour is due to different levels of the nervous system than those responsible for the perception of green and blue; and this assumption makes us suppose that the two perceptions vary as to their phylogenetic age.

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